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Uptake of perfluoroalkyl substances and halogenated flame retardants by crop plants grown in biosolids-amended soils

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ABSTRACT

The bioaccumulation behavior of perfluoroalkyl substances (PFASs) and halogenated flame retardants (HFRs) was examined in three horticultural crops and earthworms. Two species, spinach (*Spinacia oleracea*) and tomato (*Solanum lycopersicum* L.), were grown in field soil amended with a single application of biosolids (at agronomic rate for nitrogen), to represent the scenario using commercial biosolids as fertilizer, and the third crop, corn (*Zea mays*) was grown in spiked soil (~50 mg PFOS/kg soil, ~5 mg Deca-BDE/kg soil and a mixture of both, ~50 mg PFOS and ~5 mg Deca-BDE/kg soil) to represent a worst-case scenario. To examine the bioaccumulation in soil invertebrates, earthworms (*Eisenia andrei*) were exposed to the spiked soil where corn had been grown. PFASs and HFRs were detected in the three crops and earthworms. To evaluate the distribution of the compounds in the different plant tissues, transfer factors (TFs) were calculated, with TF values higher for PFASs than PBDEs in all crop plants: from 2 to 9-fold in spinach, 2 to 34-fold in tomato and 11 to 309-fold in corn. Bioaccumulation factor (BAF) values in earthworms were also higher for PFASs (4.06 ± 2.23) than PBDEs (0.02 ± 0.02).

1. Introduction

Recycling biosolids on land is recognized internationally as the most sustainable option for managing the residual sludge from urban wastewater treatment (European Economic Community, 1986, 1991a). The substantial nitrogen, phosphorus and organic carbon contained in biosolids make the spreading of this waste material on land as a crop fertilizer or an organic soil amendment suitable. An estimated 40% of the sewage sludge produced in Europe is used as a fertilizer in agriculture (European Commission, 2010). However, the recycling rates of sludge to agriculture vary greatly among European Union (EU) Member States. For example, about 1,205,000 t (dry solid) of sludge were produced in Spain during 2010, and about 995,000 t (dry solid) were recycled to agriculture, equivalent to 82% of the sludge produced (Eurostat, 2015).

Degradation and attenuation during wastewater and sludge treatment remove significant amounts of organic pollutants (Clarke and Smith, 2011). However, many of those have lipophilic properties and may be present in sewage sludges in remaining concentrations. Particular attention concerning emerging organic contaminants such as perfluoroalkyl substances (PFASs) and halogenated flame retardants (HFRs) has been given due to their widespread distribution in the environment, toxicity, and potential for bioaccumulation (Braune et al., 2014; Wen et al., 2015). The presence of PFASs and HFRs as polybrominated diphenyl ethers (PBDEs) and their alternatives decabromodiphenyl ethane (DBDPE), declorane plus (DP) and related compounds, in waste material has been documented in some countries (De la Torre et al., 2011a; Navarro et al., 2011; Ricklund et al., 2009; Sun et al., 2011). However, there is still a lack of information regarding their behavior and occurrence in the environment, but in recent years the interest in these compounds has greatly increased. For example, PFASs and PBDEs, due to their presence in biosolids, were assessed as emerging organic contaminants of potential concern for land application (Clarke and Smith, 2011). In that study, PFASs were the first compounds identified for priority attention for presenting properties that make them theoretically possible to enter human food-chain from biosolids-amended soil. Organisms are liable to take up organic contaminants and may accumulate high levels of them when they live in contaminated soil environments. Once organic compounds are introduced to the environment, two of the primary concerns for human health are the capacity for contamination of water and food. The migration of chemicals from soil to plants could facilitate a

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probable entry pathway into the food chain (Lechner and Knapp, 2011; Stahl et al., 2009, 2013; Felizeter et al., 2014). Plant uptake and distribution have been shown to be dependent on the physical-chemical properties of the chemicals, the soil and irrigation water characteristics, and the plant species and physiology, including properties such as lipid or water content and transpiration rates (Felizeter et al., 2012; Wen et al., 2013; Krippner et al., 2014; Wang et al., 2014). The study of the uptake of PFASs and HFRs by different crop plants grown in waste-amended soils provides a starting point for assessing the possible risks related to applications of biosolids to agricultural soils. Besides, organic contaminants can be taken up by organisms that live in direct contact with contaminated soil, such as soil invertebrates. The bioaccumulation of pollutants by these organisms implies a risk for earthworm population and many vertebrate species which feed on earthworms. Earthworms consume large amounts of soil and their thin cuticle is in almost constant contact with soil. If an organic contaminant is bioavailable and bioaccumulates in earthworms, it will enter the terrestrial food chain, as earthworms are eaten by many organisms from higher trophic levels. Therefore, earthworms have become common model organisms for testing toxicity and bioavailability of contaminants in soil, especially for organic compounds.

Few studies have been published detailing the behavior of organic pollutants in crops after application of contaminated sewage sludge to agricultural land. There are works describing the uptake of PFASs and PBDEs by plants in nutrient solution experiments (Felizeter et al., 2014; Krippner et al., 2014; Wang et al., 2011), from soil to plants (Stahl et al., 2009; Lechner and Knapp, 2011; Huang et al., 2011; Wang et al., 2014) from biosolids-amended soils (Yoo et al., 2011; Wen et al., 2014) and directly from undiluted biosolids (Vrkoslavová et al., 2010). These studies showed that plant accumulation of organic compounds could be dose-dependent and varied with plant species. Organofluorine compounds behave very differently to the organobromines and have unusual partitioning properties. The physical properties and molecular structures of the different compounds will likely have different effects on their accumulation in plants. Yet, although the land application of biosolids is regulated and a target value for the sum of perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) of 100 μg/kg dry mass has been established in Germany for agriculturally used sewage sludge, no EU legislation is currently in place with respect to PFASs and HFRs in biosolids (Grümping et al., 2007). Consequently, continued vigilance is required to monitor and determine the significance and implications of emerging organic compounds in land-applied biosolids.

To address this need, the main objectives of this study were: (1) to determine the transfer, bioaccumulation and distribution of selected emerging organic compounds such as PFASs, PBDEs, Dechloranes (602, 603, 604, and DP), Chlordane Plus (CP) and Mirex from biosolids-amended soil to spinach (*Spinacia oleracea*) and tomato (*Solanum lycopersicum* L.) plant under agronomic conditions. (2) to study the uptake, bioaccumulation and distribution of PFOS and BDE-209 in corn (*Zea mays*) plants under a worst case scenario. (3) to determine pollutants bioaccumulation in earthworm *(Eisenia andrei)* from contaminated soil. To the best of our knowledge, this is the first study examining PFAS uptake in spinach, PBDEs in spinach and tomato and DP uptake in crops from biosolids-amended soils.

2. Materials and methods

2.1. Study design

Three sorts of plants were chosen: spinach (*Spinacia oleracea*), tomato (*Solanum lycopersicum* L.) and corn (*Zea mays*). In spinach and tomato transfer experiments, two different organic wastes were applied to soil: anaerobically digested thermal drying sludge (W1) and anaerobically digested municipal solid waste compost (W2). The physicochemical characteristics of the soil and the two biosolids used are detailed in Table S1. Waste application rates were calculated by considering the nitrogen requirement of plants and restrictions established in the Council Directive 91/676/EEC: spinach (120 kg N/ha) and tomato (150 kg N/ha) (European Economic Community, 1991b). To represent a worst-case scenario, soils fortified by the addition of PFOS (~50 mg/kg soil, T1), Deca-BDE (~5 mg/kg soil, T2), and a mixture of both commercial mixtures (~50 and ~5 mg/kg for PFOS and Deca-BDE, respectively, T3) were used to cultivate corn plants. The experiments were performed in a climate controlled room with a light:dark cycle (16:8 h), temperature (21 ± 1 °C), humidity (55–60%), and irrigation (100 mL/d≈1000 mm/year) controlled conditions. In the spinach and corn cases the growth period consisted of 28 days, while tomato plants were exposed to amended soils for six months (time needed to reach fruiting). A total of 72 pots were used, 24 pots for each crop test (spinach, tomato and corn). Eight replicates per treatment were used for spinach and tomato whereas six replicates were used for corn. Control pots (not amended/fortified soil) and fertilizer-free pots were also prepared. After the corn experiment, ten earthworms (*Eisenia andrei*) per treatment were added to soils and a 28 days exposure study was also performed. More details are given in Supplementary material.

2.2. Sample preparation

Waste and soil samples were air-dried and processed according to methods reported previously (De la Torre et al., 2011a, 2011b, 2012; Navarro et al., 2011). Earthworms were allowed to depurate for 24 h to avoid the presence of soil particulates that could interfere with the bioaccumulation study. Plant material and earthworms were frozen and freeze-dried at low temperature (~−50 °C) for 24 h in a lyophilizer (Cryodos-50, Telstar Instrument). PFASs from spinach, tomato, corn and earthworm samples were extracted with acetonitrile by agitation, ultrasonication and centrifugation techniques. EnviCarb SPE cartridges were used to purify the extracts. For HFR determination, plant material and earthworm samples were Soxhlet extracted with hexane/acetone (50:50, v/v) and hexane/dichloromethane (50:50, v/v), respectively. Purification was accomplished using a sulphuric acid digestion and a silica column. Fractionation step was then performed in an automated purification Power Prep™ System (FMS Inc., USA). Detailed information is given in Supplementary material.

2.3. Instrumental analysis

PFASs were determined by HPLC-MS/MS (Varian 212 Liquid Chromatograph coupled to a Varian 320 triple cuadrupole MS). The chromatographic separation was carried out in an ACE C18-PFP (50×2.1 mm, 3 μm) analytical column. PBDEs were analyzed by LRMS (Agilent 6890 Gas Chromatograph connected to an Agilent 5973 MSD) for wastes and soils but in the case of biotic samples (spinach, tomato, corn and earthworms) the sensitivity of the HRMS (Micromass Autospec Ultima) was needed. In both cases chromatographic separation was performed with short and narrow capillary column (15 m×0.25 mm i.d.×0.10 μm film thickness; DB5 MS from J & W Scientific, Folson CA). Dechlorane compounds were analyzed by ECNI-MS (Agilent 5973MSD) using methane as a reagent gas. Complete details of instrumental method are described elsewhere (De la Torre et al., 2011a, 2011b; Navarro et al., 2011), see Supplementary material.

2.4. Quality assurance

Procedural blanks were processed and analyzed with every batch of samples under the same conditions. In addition, instrumental blanks consisting of methanol or nonane were run before each sample injection to check for memory effects and contamination from the LC and GC system. In the case of PFASs determination, to avoid any

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